2004

Preparation of (Pb,Ba)TiO3 Powders and Highly Oriented Thin Films by a Sol-Gel Process

Stacey Boland

Suresh Pillai

Wein-Duo Yang

Sossina Haile

Recommended Citation

Boland, S. W., et al. (2004) Preparation of highly-oriented (Pb,Ba)TiO3 thin films by a sol-gel process, *Journal of materials research*. 19, 2004, 1492-1498. doi:10.1557/JMR.2004.0199

Preparation of $(Pb,Ba)TiO_3$ powders and highly oriented thin films by a sol-gel process

Stacey W. Boland, Suresh C. Pillai, Wein-Duo Yang, and Sossina M. Haile[a)]
Department of Materials Science, California Institute of Technology, Pasadena, California 91125

(Received 17 September 2003; accepted 9 February 2004)

Solid solution $Pb_{1-x}Ba_xTiO_3$, with particular emphasis on $Pb_{0.5}Ba_{0.5}TiO_3$, was prepared using a sol-gel process incorporating lead acetate trihydrate, barium acetate, and titanium isopropoxide as precursors, acetylacetone (2,4 pentanedione) as a chelating agent, and ethylene glycol as a solvent. The synthesis procedure was optimized by systematically varying acetylacetone: Ti and H_2O:Ti molar ratios and calcination temperature. The resulting effects on sol and powder properties were studied using thermogravimetric analysis/differential scanning calorimetry, Fourier transform infrared spectroscopy, Brunauer-Emmett-Teller analysis, and x-ray diffraction (XRD). Crystallization of the perovskite structure occurred at a temperature as low as 450 °C. Thin films were prepared by spin coating on (100) MgO. Pyrolysis temperature and heating rate were varied, and the resultant film properties investigated using field-emission scanning electron microscopy, atomic force microscopy, and XRD. Under optimized conditions, highly oriented films were obtained at a crystallization temperature of 600 °C.

I. INTRODUCTION

It has recently been shown that the ferroelectric tetragonal distortion of $BaTiO_3$, in which the *a* and *c* lattice parameters differ by 1.1%, can be used for actuation.[1] Strains of approximately 0.9% have been demonstrated. Even greater strain is expected for $PbTiO_3$, which exhibits a tetragonality of 6.3%. However, this material requires a large coercive field to induce domain wall motion and is prone to brittle fracture. Solid solutions of $Pb_{1-x}Ba_xTiO_3$, or PBT, with intermediate composition will presumably present a compromise between large actuation and probability of mechanical failure. In order for PBT to be successfully used in microactuation applications and also be integrated into silicon device technology, it is necessary to synthesize high-quality epitaxial thin films at low temperatures. Furthermore, if crystallization is carried out below the Curie temperature, structural and microstructural changes associated with the cubic to tetragonal phase transition can be eliminated. Though there are several widely used techniques for fabricating oxide thin films, including physical vapor deposition, ion beam sputtering, electron beam evaporation, and pulsed laser ablation, the sol-gel method has been selected here because of its potential for low-temperature crystallization and the possibility of low-cost fabrication. In the sol-gel process, controlled hydrolysis of dissolved metalorganic precursors followed by a condensation reaction results in the formation of a three-dimensional network of particles.[2] Key challenges in the sol-gel synthesis of PBT are the identification of a solvent system in which multiple metalorganic precursors are mutually compatible and the preparation of a sol stable against uncontrolled hydrolysis. Moreover, though sol-gel and other solution techniques have widely been used for the fabrication of ferroelectric films of $PbTiO_3$ and $BaTiO_3$,[3,4] few studies of solution deposition techniques to prepare PBT thin films have been reported.[5] We present here a parametrically optimized sol-gel route for the low-temperature crystallization of powder and thin film PBT and examine the impact of various process parameters on crystallization behavior.

II. EXPERIMENTAL

A. Selection of the precursor and solvent system

Two approaches have recently been pursued in the literature as a means of crystallizing the end-member barium titanate from sol-gel methods at temperatures close to ambient. The first, demonstrated by Frey and Payne,[6] involves the use of barium and titanium alkoxides that are relatively stable against rapid hydrolysis, and therefore can be prepared with a high water to metal cation ratio (R_w) for the gelation step. The high water content apparently ensures that all metal alcohol ligands are completely replaced with metal oxygen bonds during gel formation, and all alcohol by-products are evaporated

a)Address all correspondence to this author.
e-mail: smhaile@caltech.edu
DOI: 10.1557/JMR.2004.0199

during a drying step carried out under mild heating (50–125 °C). The consequence of eliminating organic components is that barium carbonate, an intermediate product that otherwise requires high-temperature calcination for conversion to the perovskite phase, is avoided. Crystallization, using barium and titanium methoxyethoxides dissolved in 2-methoxyethanol, has been reported to occur at temperatures as low as 120 °C. The second approach, developed by Kuwabara and coworkers,[7] relies on the preparation of highly concentrated alkoxide solutions, without concern for the particular ligand group used. Such solutions yield very dense gel-structures, which, for reasons that are not entirely obvious, can then readily crystallize at low temperatures. Crystallization at temperatures as low as 50 °C has been obtained when gels (prepared as thin films) were aged under water/alcohol saturated atmospheres.

Low-temperature crystallization of the second end-member in the PBT system, lead titanate, via sol-gel methods has been explored to a much lesser extent. The most important demonstration has been that of Selvaraj et al.,[3] who obtained oriented thin-film $PbTiO_3$ from solutions of lead acetylacetonate and titanium isopropoxide in 2-methoxyethanol at temperatures as low as 425 °C. The use of lead acetylacetonate as opposed to the more typical lead acetate trihydrate apparently ensured the absence of all traces of water from the solution prior to the hydrolysis step and led to more stable gels. It is likely that the acetylacetonate ligand also served as a chelating agent for the titanium in the system, further stabilizing the system. It is not entirely obvious why stable gels should result in lower temperature crystallization.

Synthesis of PBT through sol-gel methods has been studied to an even lesser extent. Indeed, only two reports appear. Meng et al.[8] examined particle size effects on Curie temperature for sol-gel prepared materials over the entire range of $Pb_{1-x}Ba_xTiO_3$. Few synthetic details were provided, and crystallization was carried out at unspecified temperatures in the range of 500–900 °C. More recently, Giridharan and Jayavel[5] reported the synthesis of $Pb_{0.8}Ba_{0.2}TiO_3$ thin films via a sol-gel route. The starting materials were barium acetate, lead acetate trihydrate, and titanium butoxide as cation sources, acetic acid as the solvent, and 2-methoxyethanol as the chelating agent. Complete crystallization of films required calcination temperatures of approximately 650 °C (with the onset of crystallization at 400 °C), and films showed a random orientation on the Pt-coated Si and fused quartz substrates utilized. Little rationale for the particular chemical system selected was provided.

The studies of the end-member compounds suggest competing approaches to sol-gel systems that yield crystalline products at low temperatures, which cannot be simultaneously implemented: incorporation of high water content to avoid carbonate formation; preparation of highly concentrated solutions; and use of an anhydrous lead precursor. Furthermore, the precursors and solvent implied by those earlier investigations, barium methoxyethoxide, titanium methoxyethoxide, lead acetylacetonate, and methoxyethanol, were found here to be incompatible. That is, a transparent sol based on these compounds could not be prepared. In light of this initial result, an extensive survey was carried out to determine a tenable combination of metal sources, chelating agents, and solvents. Ultimately, a system in which lead acetate trihydrate, barium acetate, and titanium isopropoxide serve as metal sources, ethylene glycol as solvent, and acetylacetone as chelating agent, was the first identified for producing PBT precursor sols with good stability, relatively low crystallization temperature, and oriented thin films. A preliminary report has been presented earlier.[9]

B. Synthesis and characterization

The synthesis procedure used is depicted in Fig. 1. Barium acetate and lead acetate trihydrate were separately dissolved in ethylene glycol then mixed together to yield a clear solution. Titanium isopropoxide was dissolved in acetylacetone (the chelating agent) and ethylene glycol added to this solution. The acetate and

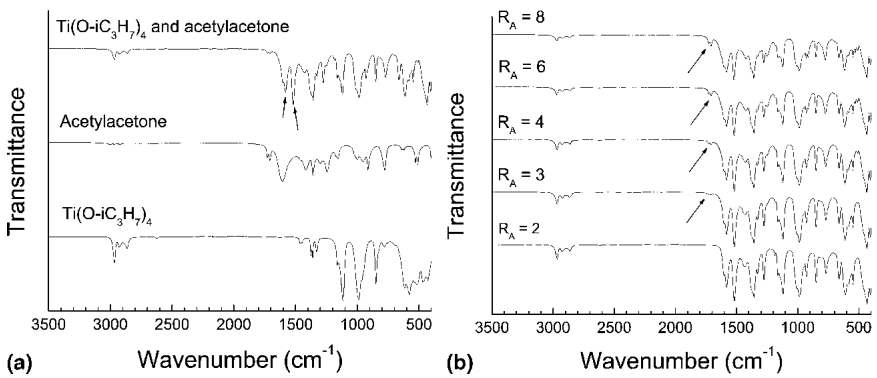

FIG. 1. FTIR spectra of (a) titanium isopropoxide, acetylacetone, and a mixture of titanium isopropoxide and acetylacetone (R_A = 4); and (b) solutions with R_A values as indicated.

alkoxide solutions were then brought together, and water introduced to the complete mixture to induce hydrolysis and condensation over the course of 1 h at 120 °C. The resultant sol was either dried to produce polycrystalline powders or spin-coated onto cleaned (100) MgO single crystals to produce thin films. MgO was selected because of its excellent lattice match to PBT and because of the possibility of incorporating biaxially textured thin-film MgO into silicon based microdevices using ion-beam-assisted deposition.[10] Between depositions, organic components from the thin films were removed by pyrolysis for three minutes. Powders and films were finally calcined in air for 2 h. The sols remain stable in sealed vials for over 1 year.

To first optimize sol chemistry and ensure complete and stable dissolution of titanium, the impact of acetylacetone:Ti molar ratio (R_A) over the range of 1–8 was examined. With an optimal value of R_A in hand, the H_2O:Ti molar ratio (R_w) and calcination temperature (T_c) used in powder synthesis were individually varied, with the goal of obtaining low-temperature, phase-pure perovskite crystallization. These parameters were varied from 2 to 32 and from 400 to 600 °C, respectively. In the case of thin films, optimal values of R_A, R_w, and T_c, as identified from the sol characterization and powder synthesis experiments, were used, and the pyrolysis temperature (T_p) and heating rate (H_R) varied from 150 to 500 °C and 1 to 20 °C/min, respectively.

The solution chemistry of the sol was probed by Fourier transform infrared (FTIR) spectroscopy using a Nicolet spectrometer over the wave number range 4000 to 400 cm^{-1}. Thermal decomposition characteristics of the oven-dried gel were studied by simultaneous differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA, Netzsch STA-449) at a constant heating rate of 10 °C/min under an argon atmosphere. Powders were examined by x-ray diffraction (XRD), Bruker D8 Discover), FTIR, and Brunauer-Emmett-Teller analysis (BET) (Gemini 2360). Thin films were examined by x-ray diffraction (Philips, X'Pert) under conventional θ-2θ geometry, but under similar scan conditions such that absolute intensities could, to a first approximation, be directly compared. Microstructural studies were carried out by atomic force microscopy (AFM, Veeco Instruments DI-3100), and carbon coated films were examined using field-emission scanning electron microscopy and energy dispersive x-ray analysis (FE-SEM/EDX, Leo Analytical).

III. RESULTS AND DISCUSSION

Introduction of acetylacetone into titanium isopropoxide is known to cause an exothermic reaction involving the replacement of isopropoxide groups by chelating acetylacetone groups. The acetylacetone group bonded to titanium prevents rapid hydrolysis by altering the condensation pathway.[11] The FTIR spectra of acetylacetone, titanium isopropoxide, and a 4:1 molar ratio of the two are presented in Fig. 2(a). The additional bands at 1590 and 1530 cm^{-1} (marked with arrows) evident in the mixed solution are assigned to acetylacetone-Ti bonding, indicating a chelated titanium precursor.[11] Sols with R_A values less than 2 were unstable against rapid precipitation, indicating the titanium precursor was not fully stabilized. Figure 2(b) shows the FTIR spectra of solutions with $R_A = 2, 3, 4, 6, 8$. The additional bands at 1700 and 1720 cm^{-1} apparent in samples with $R_A \geq 3$ indicate the presence of excess acetylacetone after chelation. Specifically, the adsorption can be attributed to the free carbonyl group (C=O) of the acetylacetone not involved in Ti chelation. The bands associated with chelated titanium (1590 and 1530 cm^{-1}, marked with an arrow) remain evident. On the basis of these results, R_A was fixed at 4 for subsequent experiments, ensuring excess acetylacetone to chelate fully titanium.

The effect of water content on the crystallization behavior of powder $Pb_{0.5}Ba_{0.5}TiO_3$ is shown in the diffraction patterns obtained from samples prepared using various R_w. All samples were prepared as in Fig. 1, using $R_A = 4$, and $T_c = 600$ °C (Fig. 3). Crystallization behavior was surprisingly insensitive to R_w, with the exception that solutions with very low water contents ($R_w \leq 2$) yielded powders of somewhat lower crystallinity than those with higher water contents. On occasion, minor amounts of secondary phases, typically pyrochlore ($Pb_2Ti_2O_6$) or barium carbonate ($BaCO_3$), were observed, as is evident in particular for $R_w = 16$ of Fig. 3. The presence or absence of these phases could not be correlated to water content, and an R_w value of 8 was selected because these sols were stable against rapid hydrolysis while sufficiently viscous to produce films of

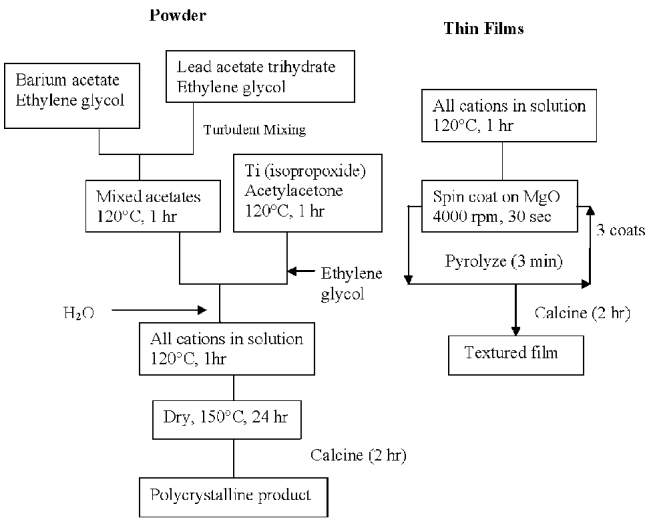

FIG. 2. Sol-gel synthesis of powder and thin film $Pb_{0.5}Ba_{0.5}TiO_3$.

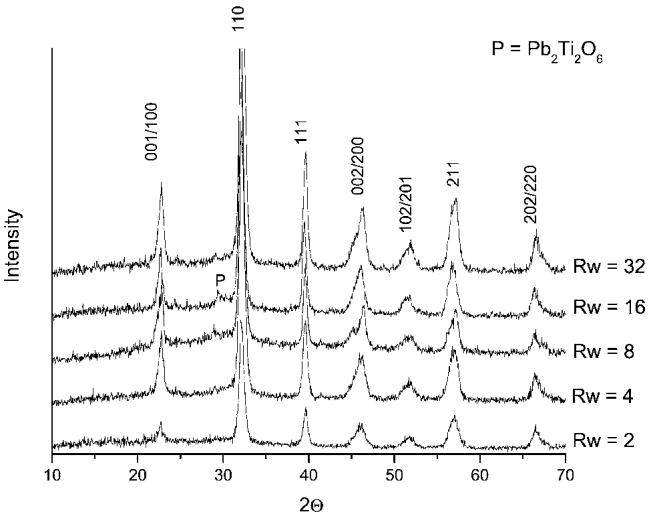

FIG. 3. X-ray diffraction patterns obtained from $Pb_{0.5}Ba_{0.5}TiO_3$ powder samples with R_w values as indicated (calcined at 600 °C, 2 h).

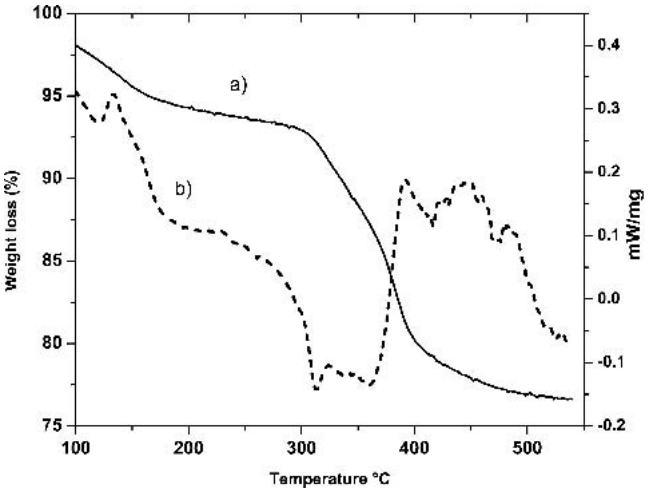

FIG. 5. (a) TGA and (b) DSC curves obtained from a $Pb_{0.5}Ba_{0.5}TiO_3$ powder sample prepared with $R_w = 8$ and $R_A = 4$.

reasonable thickness. Multipoint BET analysis showed the surface area of powders thus prepared and calcined at 500 °C was 19.98 m^2/g.

Crystallization behavior as a function of calcination temperature is presented in Fig. 4 for $Pb_{0.5}Ba_{0.5}TiO_3$ powders processed using $R_A = 4$ and $R_w = 8$. The corresponding thermal analysis data for this material are presented in Fig. 5, and FTIR data are presented in Fig. 6. Powders heat-treated at 400 °C were almost entirely amorphous (only small peaks associated with barium carbonate are present, Fig. 4). Thus, thermal events evident in the DSC data at temperatures lower than 400 °C [Fig. 5(b)] are presumably associated with weight loss. Indeed, two major weight loss events are apparent in the TGA data, the first occurring over the temperature range 100–200 °C (~10 wt%) and the second over the range 300–425 °C (~15 wt%). These two weight loss steps are likely due to the elimination of volatile by-products and solvents (boiling point of ethylene glycol = 190 °C) and to the removal of acetate groups from the metalorganic precursors, respectively.[12] Both events are accompanied by exothermic peaks in the DSC data, and weight loss appears complete by 450 °C. At 450 °C, the diffraction data show crystallization of the perovskite phase along with a secondary pyrochlore phase (Fig. 4). As expected, crystallinity increased with increasing temperature. By 500 °C, the diffraction data are dominated by the perovskite phase, although small peaks due to barium carbonate are still present. Complete crystallization of an impurity-free perovskite phase was obtained at 550 °C. Crystallization events are evident in the DSC curve, Fig. 5(b), at temperatures of 425 and 480 °C, with

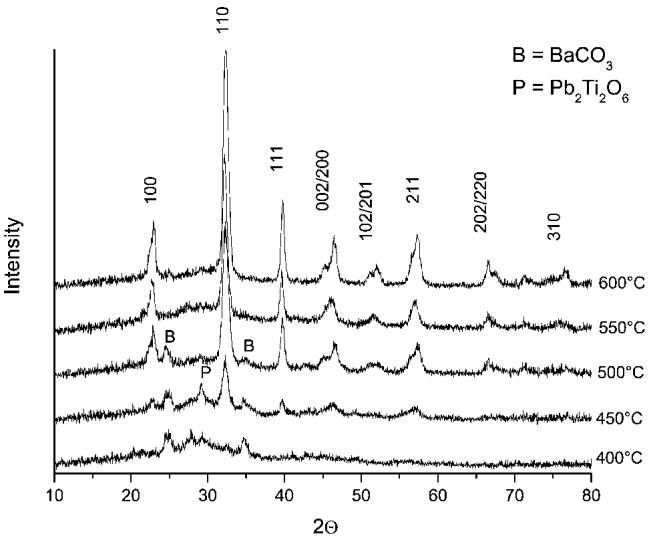

FIG. 4. X-ray diffraction patterns obtained from $Pb_{0.5}Ba_{0.5}TiO_3$ powder samples calcined at the temperatures indicated ($R_w = 8$, $R_A = 4$).

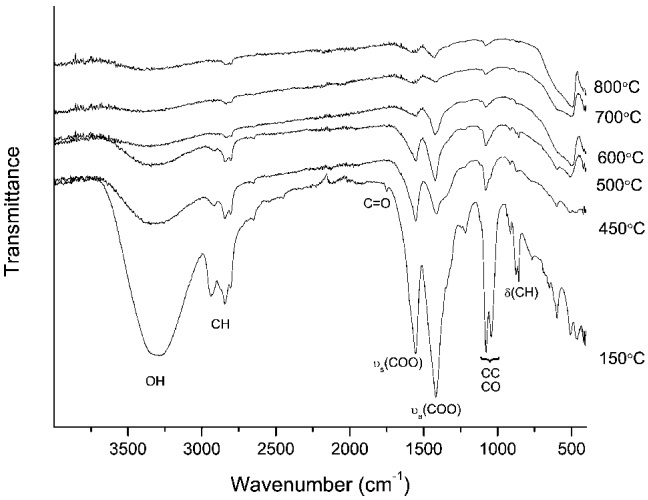

FIG. 6. FTIR spectra of $Pb_{0.5}Ba_{0.5}TiO_3$ powders with varied calcination temperatures (T_c = 150, 450, 500, 600, 700, 800 °C).

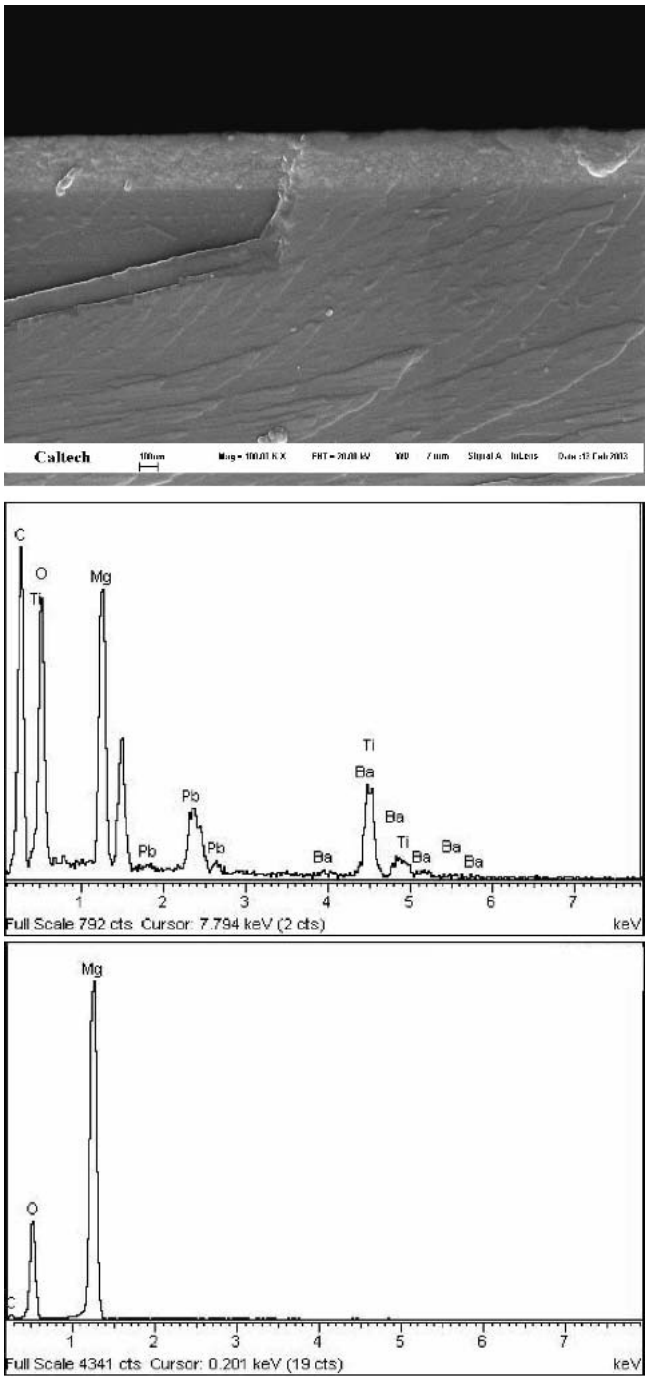

FIG. 7. Cross-sectional analysis of $Pb_{0.5}Ba_{0.5}TiO_3$ thin film: (a) FE-SEM, (b) EDX of film, and (c) EDX of substrate (note: cross section was coated in carbon for enhanced detail).

the possible onset of a third event at 540 °C, the highest temperature examined.

The thermal analysis data presented in Fig. 5 for powders prepared with $R_w = 8$ was typical of all samples, irrespective of water content (from $R_w = 2$ to 32). Total weight losses (to ~500 °C) were 25–30 wt%. One might have expected decreasing weight loss with increasing R_w

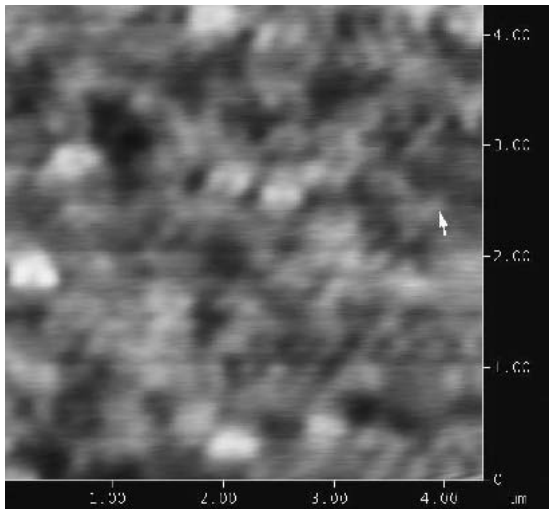

FIG. 8. Two-dimensional AFM surface scan ($R_A = 4$, $R_w = 8$, $T_c = 600$ °C, $T_p = 450$ °C, $H_R = 5$ °C/min, $x = 0.5$).

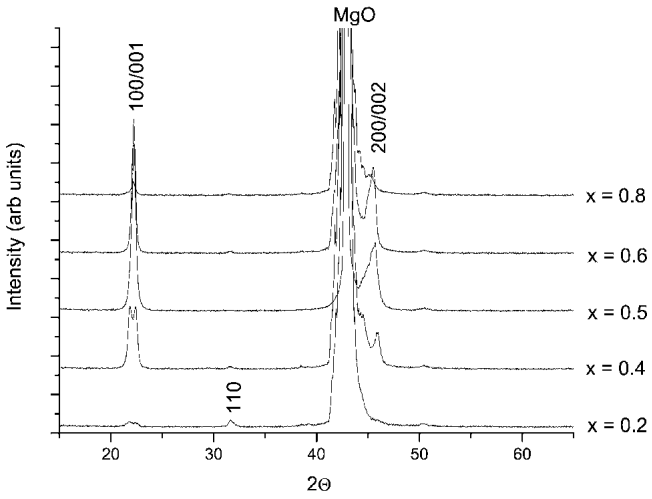

FIG. 9. X-ray diffraction patterns obtained from $Pb_{1-x}Ba_xTiO_3$ films with compositions as noted ($R_A = 4$, $R_w = 8$, $T_p = 450$ °C, $T_c = 600$ °C, $H_R = 5$ °C/min).

as a consequence of the resultant gel containing fewer organic groups as hydrolysis proceeds to greater extents.[6] It has been reported, however, that even a large excess of water ($R_w = 20$) does not fully hydrolyze the acetylacetone ligands bonded to titanium,[11] and this may be responsible for the observed results.

The majority of the adsorption bands in the FTIR spectrum of the dried gel ($T_c = 150$) could be readily associated with the various organic moities in the sol.[13–15] (Fig. 6) and are directly identified on the figure. Most of the peaks associated with the original reagents are significantly diminished by 450 °C, in agreement with DSC/TGA and XRD data discussed previously. Powders calcined at ≥500 °C show Ti–O vibrations (497 cm^{-1}).[15] At 700 °C, the band around 3300 cm^{-1} (OH group due to ethylene glycol and isopropanol) is significantly weakened, and bands around 1500 cm^{-1} and 1400 cm^{-1}

(COO symmetric and antisymmetric stretching from the acetates) continue to decrease in intensity. The band around 500 cm^{-1} (Ti–O vibrations) strengthens as temperature increases from 500 to 800 °C. This correlates well with observed XRD data, which show increasing crystallinity of the perovskite phase through those temperatures. The FTIR data suggest bond changes are minimal for calcination temperatures ≥600 °C. Calcination of thin film samples was accordingly carried out at T_c = 600 °C.

All thin films were synthesized using the optimized parameters R_A = 4, R_w = 8, and T_c = 600 °C, and for an initial investigation of the influence of pyrolysis temperature, the heating rate H_R was fixed at 5 °C/min. Diffraction patterns and scanning electron microscopy images were obtained for films processed using pyrolysis temperatures (T_p) in the range from 150 to 450 °C and then calcined to 600 °C. The diffraction patterns (not shown) revealed that all films were well-crystallized and highly (001)-oriented, with higher pyrolysis temperatures leading to slightly improved phase purity and degree of orientation. The FE-SEM images (not shown) furthermore demonstrated that all films, regardless of pyrolysis temperature, were crack-free. Treatment of films at pyrolysis temperatures higher than 450 °C, and even subjecting them to complete calcination between depositions, provided no tangible benefit. Thus, T_p = 450 °C was chosen for use in further experiments. Given that perovskite crystallization initiates at approximately 450 °C (Fig. 4), it is quite possible that some PBT nuclei form at the MgO interface even during the short pyrolysis step and serve as templates for PBT growth under full calcination conditions.

The influence of the heating rate (H_R) used to reach the calcination temperature was investigated for samples pyrolyzed at 450 °C and calcined at 600 °C. The XRD data (not shown) revealed that heating rates of 1–20 °C/min all lead to highly oriented, phase-pure perovskite thin films. A value of 5 °C/min was selected simply for ease.

Film thickness was generally sensitive to the deposition parameters explored. In the case of films deposited under optimized conditions, cross-sectional FESEM showed that each layer was 70 ± 7 nm thick [Fig. 7(a)]. Chemical analysis by energy dispersive x-ray (EDX), indicated the presence of lead, barium and titanium in the film [Fig. 7(b)] and magnesium and oxygen in the substrate [Fig. 7(c)], confirming that the light region in the image is indeed the PBT film. Examination of a 4-μm × 4 μm AFM surface scan showed the film had a surface roughness of 1.05 nm with average grain size (diameter) of 113 nm (Fig. 8). Particle size effects have been observed for both $BaTiO_3$ and $PbTiO_3$ in samples with similarly sized grains and may be of relevance here. In particular, reduction of particle size typically favors the cubic, paraelectric phase and lowers the ferroelectric transition temperature.[8] Accordingly, it may be necessary to develop schemes for inducing grain growth in these films to ultimately achieve the goal of direct crystallization of the tetragonal phase.

Using the optimized parameters (R_A = 4, R_w = 8, T_p = 450, T_c = 600, H_R = 5 °C/min), a range of solid solution $Pb_{1-x}Ba_xTiO_3$ was synthesized with x = 0.2, 0.4, 0.5, 0.6, 0.8 (Fig. 9). Although the synthesis conditions were optimized for x = 0.5, oriented films were obtained for all but the highly lead rich sample (x = 0.2); only very weak (110) peaks are present for x = 0.4, 0.6, and 0.8. For samples containing more than 50% Pb, tetragonal splitting is evident in the diffraction patterns and is expected given that the difference between the *a* and *c* lattice parameters of the end-member lead titanate is six times greater than that of the opposite end member, barium titanate. The peak splitting is most apparent for the x = 0.4 sample. The reasons for the misorientation and low peak intensity of the sample containing the greatest lead content (x = 0.2) are not obvious, but are likely related to the large structural change associated with the cubic to tetragonal phase transition as the sample is cooled through its Curie temperature and the tendency of Pb to volatilize at high temperature.

IV. CONCLUSIONS

A sol-gel process suitable for depositing thin film PBT beginning with lead acetate, barium acetate, and titanium isopropoxide was developed and parametrically optimized. To chelate fully titanium, the optimal value of R_A (acetylacetone to titanium molar ratio) was determined to be 4. Crystallization behavior was surprisingly insensitive to the water content of the system over the range of water to titanium molar ratios, R_w, from 2 to 32. A value of 8 provides the appropriate balance between sol stability and viscosity. Under these conditions, perovskite crystallization occurred at a temperature as low as 450 °C, albeit in the presence of impurity phases. Single-phase (powder) PBT was obtained at 550 °C. Deposition of the sol by spin coating on (100) MgO resulted in highly oriented PBT films, with mixed (001)/(100) orientation. A short pyrolysis (3–5 min) at 450 °C was found to be sufficient to remove adequately volatile organics between layer deposition and produce films of equal quality to those fully calcined between deposition steps. Heating rate during calcination was found to have little influence on film orientation. Films prepared using these parameters had layer thickness of ~70 nm, a surface roughness of 1.05 nm, and an average grain size of 113 nm. Further optimization may enable crystallization below the Curie temperature and avoid the structural and microstructural changes induced by the transition, particularly for high Pb content compositions.

ACKNOWLEDGMENTS

The authors gratefully acknowledge Dr. Chi Ma for his assistance with electron microscopy and Justin S. Boland for his help with atomic force microscopy. This work has been funded by a United States Department of Defense MURI award administered by the Army Research Office. Additional support has been provided by the National Science Foundation, through the Caltech Center for the Science and Engineering of Materials.

REFERENCES

1. E. Burcsu, G. Ravichandran, and K. Bhattacharya, *Appl. Phys. Lett.* **77,** 1698 (2000).
2. R.J.P. Corriu and D. Leclercq, *Angew. Chem. Int. Ed. Engl.* **35,** 1420 (1996).
3. U. Selvaraj, A.V. Prsadarao, and S. Komerneni, *Mater. Lett.* **20,** 71 (1994).
4. H. Nishizawa and M. Katsube, *J. Solid State Chem.* **131,** 43 (1997).
5. N.V. Giridharan and R. Jayavel, *Mater. Lett.* **52,** 57 (2002).
6. M.H. Frey and D.A. Payne, *Chem. Mater.* **7,** 123 (1995).
7. M. Kuwabara, S. Takahashi, and T. Kuroda, in *Better Ceramics Through Chemistry V*, edited by M.J. Hampden-Smith, W.G. Klemperer, and C.J. Brinker (Mater. Res. Soc. Symp. Proc. **271,** Pittsburgh, PA, 1992), p. 365.
8. J.F. Meng, R.S. Katiyar, and G.T. Zou, *J. Phys. Chem. Solids* **59,** 1191 (1998).
9. W-D. Yang, S.C. Pillai, S.W. Boland, and S.M. Haile, in *Ferroelectric Thin Films XI*, edited by D.Y. Kaufman, S. Hoffmann-Eifert, S.R. Gilbert, S. Aggarwal, and M. Shimizu (Mater. Res. Soc. Symp. Proc. **748,** Warrendale, PA, 2002) U12.21.1-6.
10. R.T. Brewer, D.A. Boyd, M. El-Naggar, S.W. Boland, S.M. Haile, D.G. Goodwin, and H.A. Atwater, (204th Mtg. Electrochem. Soc., Orlando, FL, Oct. 2003).
11. C.J. Brinker and G.W. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing* (Academic Press, New York, 1990), p. 59.
12. R. Caruso, O. de Sanctis, A. Frattini, C. Steren, and R. Gil, *Surf. Coat. Technol.* **122,** 44 (1999).
13. H.K. Park, D.K. Kim, and C.H. Kim, *J. Am. Ceram. Soc.* **80,** 743 (1997).
14. H.K. Ryu, J.S. Heo, S. Chao, and S.H. Moon, *J. Electrochem. Soc.* **146,** 1117 (1999).
15. K. Kitaoka, H. Kozuka, and T. Yoko, *J. Am. Ceram. Soc.* **81,** 1189 (1998).